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(19) (CA) **CANADIAN PATENT** (12)

(54) Removal of Nitrogenous Compounds from Petroleum Processing Products Using Bromine-Treated Ilmenite

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Abstract:

A process is described for removing nitrogen compounds from petroleum processing liquid products and synthetic fuels. According to the novel feature, ilmenite pretreated with a halide, such as bromine, is used as adsorbent for the nitrogen compounds.

Removal of nitrogenous compounds from petroleum processing products using bromine-treated ilmenite

This invention relates to a process for removing nitrogen compounds from hydrocarbon oils. More particularly, it relates to a process for removing dissolved organic nitrogen compounds from synthetic fuels.

Almost all petroleum crude oils contain small amounts of various nitrogenous compounds which may be found in varying concentrations in the fractions and products produced from such crudes. The nitrogenous components in bitumens, heavy oils and synthetic fuels pose problems for recovery and processing operations. These compounds, together with the associated polar materials, are responsible for the emulsion problems encountered in hot water separation processes of bitumen from sand. They also have a very deleterious effect on refinery catalysts used in upgrading processes.

The presence of nitrogenous compounds in fractions and products produced is also disadvantageous and, if present in fuel products, tend to cause color change, organic sediment formation upon storage, etc. The nitrogen content of synthetic fuels is extremely important to the refiner because nitrogen is harder to remove than other heteroatoms, e.g., sulfur and oxygen.

Various procedures have been known for removing nitrogenous compounds, e.g. using ion-exchange resins or complexing with transition metal salts. For instance, U.S. Patent 3,005,826 describes the use of a silica-gel adsorbent for removing organic nitrogen components, and

other adsorbents for this purpose are described in U.S. Patent 3,055,825. A major problem with the commercial ion exchange resins is that they are relatively expensive and do not tend to adsorb neutral nitrogenous compounds. Complexing with transition metal salts usually requires severe treating conditions with resultant high material loss. In Poirier et al, Canadian application serial No. 421,286 filed February 10, 1983 there is described the use of chlorosilylated silica gel for the removal of nitrogenous materials from liquid hydrocarbons.

According to the present invention it has been found that ilmenite pretreated with a halide selected from chlorine, bromine and fluorine is a highly effective adsorbent for the removal of nitrogenous compounds from petroleum processing liquid products.

Ilmenite is a titanium ore which is quite abundant throughout the world and relatively inexpensive. It typically has the chemical composition $FeTiO_3$. For treatment with a halide, crushed ilmenite is treated with an excess of halide, preferably under heating. The halide is preferably bromine. After treatment, the ilmenite is washed and dried.

The optimum particle size for the halide-treated ilmenite adsorbent will depend upon the manner in which it is used in the process, i.e. as a fixed compact bed, a fluidised bed, etc., but is usually between about 2 and about 400 mesh (Canadian Standard Sieve).

The nitrogen-containing liquid hydrocarbons may be contacted with the halide-treated ilmenite in either the vapor or liquid phase. The pressure is usually near atmospheric, but may be either sub-atmospheric or super-atmospheric. The adsorption may be carried out at moderate temperatures and typically at room temperature.

The invention will be more readily understood from the following illustrative examples:

Example 1

A. A bromine treated ilmenite was prepared using as starting material an ilmenite ore taken from a deposit in the St. Urbain region of Quebec, Canada. This ore had the following elemental analysis:

TABLE I

Constituent	wt %
TiO_2	38.70
Fe_2O_3	18.64
FeO	28.66
SiO_2	4.27
Al_2O_3	4.80
MgO	4.80
CaO	0.50
MnO_2	0.16
Na_2O	0.05
V_2O_5	0.16
Cr_2O_5	0.08
NiO_3	0.10
CuO	0.04
BaO	0.01

The ilmenite ore was crushed to about 200 mesh size (Canadian Standard Sieve) and 15 g of the crushed ilmenite were placed in a 100 mL round bottom flask equipped with a reflux condenser. An excess of bromine (about 10 mL) was added. This mixture was heated at 58°C for two hours and then the mixture was cooled down and the excess bromine washed away with 50 mL of pentane. The treated ilmenite was filtered and then washed again with pentane until the solvent became colorless. The treated ilmenite was then dried with a stream of nitrogen and used as an adsorbent.

B. The petroleum processing liquid product used was a coker kerosene obtained from The Great Canadian Oil Sands plant and had the following typical properties:

TABLE 2

Boiling range,	°C	193-279
Specific Gravity,	60/60 °F	0.871
Sulphur,	wt %	2.32
Nitrogen,	ppm	430
Pour Point,	°F	Below -60
Cloud Point,	°F	Below -60
Flash Point,	°F	116
Vanadium,	ppm	0.40
Nickel,	ppm	0.36
Iron,	ppm	0.59
Ramsbottom Carbon Residue (10% bottoms)	wt %	0.29
Aromatics and Olefins,	vol %	58
Saturates,	vol %	42

C. Two extraction columns were set up, one containing regular crushed ilmenite and the other containing the above bromine-treated crushed ilmenite. Each column was packed with 10 grams of the sorbent material.

120 mL of coker kerosene was percolated through each column and eight fractions of the eluate were collected (two-5 mL and six-10 mL fractions) and analyzed for total nitrogen. The nitrogen determinations were obtained using a Dohrmann micro-coulometer Model C-200B.

The results of nitrogen removal were compared and are shown in Table 3 below:

TABLE 3

Nitrogen content of coker kerosene feed - 430 ppm

Fraction	Volume (mL)	% Total Nitrogen Removal	
		Ilmenite	Treated Ilmenite
1	5	17.3	98.1
2	5	16.6	90.2
3	10	14.7	84.5
4	10	19.7	71.0
5	10	15.2	50.2
6	10	18.6	43.8
7	10	13.3	39.3
8	10	12.1	35.9

From the above results it will be seen that while the untreated ilmenite was ineffective for removing nitrogen from coker kerosene, ilmenite treated with bromine was quite efficient for removing the nitrogenous material.

Claims:

1. A process for removing dissolved organic nitrogen compounds from liquid hydrocarbons, which comprises contacting the liquid hydrocarbons with an adsorbent comprising particles of ilmenite treated with a halide selected from chlorine, bromine and fluorine and thereafter separating the hydrocarbons from the adsorbent.

2. The process according to claim 1 wherein the halide is bromine.

3. The process according to claim 1 wherein the ilmenite has a particle size in the range of about 2 to 400 mesh.

4. The process according to claim 1, 2 or 3 wherein the liquid hydrocarbons are petroleum processing liquid products.

5. The process according to claim 1, 2 or 3 wherein the liquid hydrocarbons are obtained from processing bitumen or heavy oil.

6. The process according to claim 1, 2 or 3 wherein the liquid hydrocarbons are petroleum distillate fractions.

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